

There are fundamental differences between the instant invention and the invention of Shen et al. The instant invention is directed toward controlling the etch rate for an etching solution used to dissolve a solid material, such as a semiconductor wafer (typically silicon, silicon oxide, or another silicon compound), whereas the Shen et al. invention is directed toward controlling the quality of a stripper solution used to dissolve organic photoresist films from the surface of the semiconductor wafer. The instant invention utilizes near infrared radiation to detect inorganic etchant species (for example, HF , F^- , HF_2^- , H^+ and OH^-), whereas the Shen et al. invention uses infrared radiation to detect organic photoresist materials. Although there is some overlap between the wavelength ranges for the near infrared radiation (700 – 2500 nm) used in the instant invention and the infrared radiation (2000 – 15,000 nm) used by Shen et al., the inorganic species detected in the instant invention and the organic species, typically containing ketene and ester groups (see Fig. 2), detected by Shen et al. tend to absorb radiation of significantly different wavelengths. The results of the instant invention are typically used to adjust the concentration of the etchant species to provide a desired and/or known solid etch rate, whereas the results of the Shen et al. invention are used to determine when accumulated photoresist materials from photoresist stripping need to be removed from the stripper solution.

Because of such fundamental differences, the invention of Shen et al. cannot be applied to provide the etch rate of semiconductor wafers, for example, in an etchant solution, as provided in the instant invention. In particular, the inorganic etchant species used to etch semiconductor wafers and other solids do not absorb radiation in the infrared wavelength region used by Shen et al. In addition, a simple threshold radiation absorption, as employed by Shen et al. to detect photoresist species in stripper solution, cannot provide a semiconductor etch rate, which is determined by several etchant species in equilibrium in the etchant solution. Shen et al. did not disclose measurement of even the photoresist stripping rate.

A key difference with respect to patentability is that the independent claim (Claim 14) of the instant application requires that a “rate of etching of said solid” be provided, which is a limitation not required by Shen et al. Furthermore, the apparatus claimed by Shen et al. (Claim 1) comprises a tank with two sections, as well as two filters for filtering photoresist materials accumulated in the stripper solution. Neither a separated tank nor filters are required to practice the instant invention. There are no method claims for the Shen et al. patent. It is clear that the

patent of Shen et al. describes an invention that is patentably distinct from that of the instant invention.

Based on the arguments given above, independent Claim 14, as amended, should be allowed as patentably distinct. Claims 15-16, 18, 21-24, 26, 28, 32 and 33 are all dependent claims and should be allowed if the parent claim (Claim 14) is allowed. Nonetheless, the following comments with respect to the dependent claims are in order.

With respect to Claim 15, the infrared spectral range disclosed by Shen et al. differs from the near infrared range disclosed in the instant application.

With respect to Claim 16, Shen et al. utilize only the “level of intensity” of the detected radiation (Column 2, lines 46-49) and do not perform a chemometric manipulation.

With respect to Claim 18, Shen et al. do not teach that the algorithm provides a rate of depletion of a chemical component.

With respect to Claims 22-24, Shen et al. do not teach “that the comparing step comprises converting one optical property into a concentration rate of change of at least one chemical component”.

With respect to Claim 26, Shen et al. do not teach “detecting a fault in a rate of addition of a replenishing component”. Column 4, lines 38-44 describe use of a detected optical signal to indicate the need for corrective action to remove accumulated photoresist materials (not to replenish a component).

With respect to Claim 28, Shen et al. do not teach a method that is independent of temperature and the presence of bubbles.

With respect to Claim 32, Shen et al. do not teach determining a concentration of an acid.

With respect to Claim 33, Shen et al. teach use of an infrared light source (2000 – 15,000 nm wavelength) but do not teach use of the near infrared light source (700 – 2500 nm wavelength) used for the instant invention.

Claim Rejections - 35 USC §103

Claims 14-26, 28 and 30-33 were rejected under 35 USC 103(a) as being unpatentable over the publication “In-Situ Chemical Concentration Control for Wafer Wet Cleaning” to Brause et al. in view of the publication “Quantification of Hydrofluoric Acid Species by

Chemical Modeling Regression of Near-Infrared Spectra” to Thompson et al.

As indicated by the examiner, Brause et al. teach the use of conductivity measurements to control the concentrations of hydrofluoric acid (HF) etching solutions (and RA cleaning solutions) used in semiconductor wafer fabrication processes. Brause et al. actually teach away from the instant invention by stating that the silicon oxide “etch rate depends on HF acid concentration” (page 24, second column, second paragraph, lines 5-6) and “methods available today...include near infrared (NIR) spectroscopy” and have “major drawback...that they are used only on a ‘stand-alone’ basis and frequently are quite expensive. Compact instrumentation and full integration of these techniques into the process baths have had limited success” (page 24, second column, third paragraph). Contrary to these teaching, the present inventors recognized that semiconductor etch rates in HF etchant solutions depend on several species (principally, HF, F⁻, HF₂⁻, H⁺ and OH⁻) that provide different etch rates and are present in equilibrium (see paragraphs [0250]-[0255] of the instant application), so that a more incisive analytical method than conductivity was needed to control the etch rate of wafer etchant solutions. Also, contrary to the teachings of Brause et al., the present inventors have been successful in fully integrating the NIR method with the wafer etching process.

As indicated by the examiner, Thompson et al. teach that NIR spectroscopy may be used to detect HF species in aqueous solution. Thompson et al. used NIR radiation of relatively short wavelength in conjunction with spectrophotometric titration and multivariate model-based regression analysis (see publication abstract) in an attempt to provide detection of each of the species known to be involved in HF equilibria in aqueous solution (HF, F⁻, HF₂⁻, H⁺ and OH⁻). Although “ambiguities in the equilibrium constants and concentration estimates were observed” (page 34, column 2, last paragraph), Thompson et al. stated “The measurement scheme presented in this paper should be adaptable for process measurements” (page 35, first column, second paragraph). However, they provided no suggestion concerning the type of adaptation that would be required, and the use of the word “should” indicates doubt by the authors that such an adaptation could be made. That this doubt was very significant is indicated by the statement by Thompson et al. “Our results appear consistent with the commonly accepted model for HF dissociation. However, ...the intensities of the reconstructed spectra depend on the concentration range studied. This is yet another manifestation of the ill-posed nature of this analysis, which is

only partially alleviated by model-based regression.” This statement definitely teaches away from use of NIR for controlling HF etchant solutions. This is particularly true considering that Thompson et al. performed an academic study under well-defined conditions, and did not investigate real-world etchant solutions, which are dynamic and often contain interfering byproduct species. Thus, both Brause et al. and Thompson et al. teach away from the instant invention, which involves use of NIR spectroscopy to control etching processes for semiconductor wafers and other solids.

The present inventors were the first to recognize that, because the semiconductor wafer etching process involves complex equilibria of etchant species providing differing etch rates, effective process control is best provided by relating the composite NIR spectrum to the etch rate via chemometric analysis (without complete deconstruction of the spectrum into its individual components). Neither of the references cited make any suggestion of such an approach, and in fact teach away from the use of NIR for control of wafer etching processes.

Based on the arguments presented above, independent Claim 14 should be allowed so that all of the dependent claims should be allowed. Nonetheless, the following comments with respect to the dependent claims are in order.

Regarding Claim 18, Thompson et al. studied only laboratory solutions via spectrophotometric titrations and did not investigate the rate of depletion, which is typically associated with a production process.

Regarding Claim 22-24, Thompson et al. studied only laboratory solutions via spectrophotometric titrations and did not investigate a concentration rate of change, which is typically associated with a production process.

Regarding Claim 26, Thompson et al. studied only laboratory solutions via spectrophotometric titrations and did not detect a fault in a rate of addition of a replenishing chemical component.

Claims 27 and 29 were rejected under 35 USC 103(a) as being unpatentable over the publication “In-Situ Chemical Concentration Control for Wafer Wet Cleaning” to Brause et al. in view of the publication “Quantification of Hydrofluoric Acid Species by Chemical Modeling Regression of Near-Infrared Spectra” to Thompson et al. and in further view of JP 63307334 A to Nogami.

Claims 27 and 29 are dependent claims and should be allowed if the parent claim (Claim 14) is allowed, which should be the case based on the arguments presented above.

LISTING OF CLAIMS

1. (withdrawn)
2. (withdrawn)
3. (withdrawn)
4. (withdrawn)
5. (withdrawn)
6. (withdrawn)
7. (withdrawn)
8. (withdrawn)
9. (withdrawn)
10. (withdrawn)
11. (withdrawn)
12. (withdrawn)
13. (withdrawn)
14. (currently amended) A method for real-time dynamic analysis of chemical etching of a solid in a liquid etchant, comprising the steps of:

passing electromagnetic radiation from an electromagnetic radiation source through a said liquid etchant, at at least at two points in time, wherein said liquid etchant is operative to etch said solid;

performing ex situ non-contact scanning detection over a predetermined spectral range of said electromagnetic radiation passed through said liquid etchant, by means of a detector over said at least at two points in time so as to detect at least one change in at least one optical property of said liquid etchant; and

comparing said at least one change in said at least one optical property at said at least two points in time by means of an algorithm in a processor so as to provide a rate of etching of said solid.

15. (original) A method according to claim 14, wherein said passing includes:

i) emitting electromagnetic radiation in said predetermined spectral range from an electromagnetic radiation source;

ii) transmitting said electromagnetic radiation via a first optical transmission element from said electromagnetic radiation source through a sampling element containing a sample of said liquid etchant; and

iii) conveying output electromagnetic radiation from said sample of said liquid etchant via a second optical transmission element to said detector.

16. (original) A method according to claim 14, wherein said comparing further comprises performing a chemometric manipulation on data relating to said at least one change in said at least one optical property.

17. (original) A method according to claim 14, wherein said algorithm further provides a differential rate of change of said etching of said solid over a period of time.

18. (original) A method according to claim 14, wherein said algorithm further provides a rate of depletion of at least one chemical component of said liquid etchant over a period of time.

19. (original) A method according to claim 14, wherein said algorithm further provides a rate of etching of said solid as a function of a concentration of said liquid etchant.

20. (original) A method according to claim 14, wherein said liquid etchant comprises ions selected from the group consisting of halide ions, sulfuric ions, sulfurous ions, nitrous ions, nitric ions, and nitride ions.

21. (original) A method according to claim 14, wherein said passing further comprises passing said liquid etchant through a sampling element having a substantially transparent sampling tube.

22. (original) A method according to claim 14, wherein said comparing step further comprises converting said at least one change in said at least one optical property of said liquid etchant into a concentration parameter of at least one chemical component of said liquid etchant.

23. (currently amended) A method according to claim 14, wherein said comparing step further comprises ~~further comprises~~ providing a concentration of at least one chemical component of said liquid etchant.

24. (original) A method according to claim 23, wherein said comparing step further comprises supplying a rate of change of a concentration of said at least one chemical component.

25. (currently amended) A method according to claim 14, further comprising:

a) obtaining a plurality of liquid etchant samples, wherein each sample of said plurality of liquid etchant samples has a known etch rate;

b) irradiating said plurality of liquid etchant samples with NIR and recording their respective spectral scanning transmission intensities over said predetermined spectral range;

c) comparing variations of their respective spectral scanning transmission

intensities over said predetermined spectral range so as to correlate spectral transmission of said plurality of samples with said known etch rate, wherein said known etch rate is determined by thickness measurements;

d) developing a calibration model based on the results of step (c); and

e) measuring scanning spectral transmission over said predetermined spectral range of a further liquid etchant sample so as to determine at least one of an etch rate and a concentration of said ~~at~~ further liquid etchant based on said calibration model.

26. (original) A method according to claim 14, further comprising detecting a fault in a rate of addition of a replenishing chemical component of said liquid etchant.

27. (original) A method according to claim 14, wherein said comparing step further comprises detecting a bubble in said liquid etchant.

28. (original) A method according to claim 14, wherein said comparing step further comprises determining a concentration of at least one of a plurality of chemical components in said liquid etchant with a confidence level of more than 95%.

29. (original) A method according to claim 28, wherein said method is independent of a presence of bubbles in said liquid etchant.

30. (original) A method according to claim 28, wherein said method is independent of the temperature of said liquid etchant.

31. (currently amended) A method according to claim 14, further comprising the steps of:

applying computer software to data relating to said at least one change in said at least one optical property so as to provide an updated algorithm; and

applying said updated algorithm to data ~~of~~ relating to a new sample of said liquid etchant so as to further provide a rate of etching of said solid in said new sample.

32. (original) A method according to claim 14, further comprising determining a concentration of at least one of the following: HF:H₂O, HF1:5, HF1:50, BOE, H₂SO₄:HNO₃:HF, EG+HF, Acetic Acid: NH₄F, H₃PO₄:HNO₃:Acetic acid, HNO₃:HF, an acid, a base, a commercial oxide etchant, a commercial silicon etchant, a commercial metallic etchant, H₂SO₄:H₂O₂, H₂SO₄:HNO₃ and H₂SO₄:persulfate.

33. (original) A method according to claim 14, wherein said predetermined spectral range is in a near infrared range (700-2500 nm).

CONCLUSIONS

It is respectfully requested that all of the pending claims, as amended, of the present application be allowed.

Respectfully submitted,



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